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Electronic spectrum of octaazacubane (N_8)

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Abstract : MRINDO/S calculation augmented by singly-excited configuration interaction was performed on octaazacubane. We report ionization potentials, singlet and triplet excitations and the singlet-triplet splittings in octaazacubane. The importance of outer (Rydberg) atomic orbitals is stressed and it is found that none of the transitions leads to an excited state with considerable Rydberg character.

Keywords : Octaazacubane, ionization potentials, electronic spectrum.

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By use of *ab initio* self-consistent-field (SCF), coupled cluster and many-body perturbation theory (MBPT) methods, the octahedral nitrogen molecule N_8 is found to be in a metastable state, corresponding to local minimum on its potential energy surface [1]. The potential existence of more exotic metastable species offers insight into nature of the chemical bond. For example, the possible metastable molecules include three forms of N_3H_3 analogous to propane, cyclopropane and ozone (experimentally known [2]) and the cubane analogue N_8.

Lauderdale *et al* [1] studied the bonding and stability of N_8. They opine that synthesis of metastable molecules would offer a potential route towards the storage of large amount of energy. A great deal of efforts has been focussed on increasing density by producing highly strained molecular systems. One way of further increasing the energy of these systems is to replace each CH fragment with an N atom. In the limit of full replacement, nitrogen analogues of tetrahedrane N_4 and cubane N_8 are obtained. While one would expect these molecules to be thermodynamically unstable, pathways for decomposition to ground state N_2 are forbidden by orbital symmetry. Therefore, it is possible that N_4 and N_8 can be observed experimentally [1].

Lauderdale *et al* [1] argue that while each of these three molecules (N_4, N_6, and N_8) has been studied in the past [3–15], the effects of electron correlation have not been thoroughly explored. Furthermore, little attention has been paid to characterizing minimum by the calculation of second derivatives. Without this critical piece of information, any discussion of thermodynamical stability is doubtful.

Trinquier *et al* [8] looked at tetrahedral X_4 and cubane X_8 structures of N, P, and S using SCF pseudopotential calculations. They found N_8 to be much less stable (thermodynamically) than $2N_4$. They concluded that all X_8 systems are generally less stable. Engelke *et al* [15] optimized the N_8 geometry at the SCF level using STO-3G, 4-31G, and 4-31G* basis sets. They found N_8 configuration to be stable minimum with each basis set

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by determining the harmonic frequencies and concluded that since the lowest mode was relatively strong, the molecule would be difficult to deform. No structures were determined and characterized at the correlated level. However, Lauderdale *et al*[1] investigated octaazacubane (N_8) including correlated predictions of vibrational frequencies.

Leininger *et al* [16] using *ab initio* molecular electronic spectrum methods examined three isomers of N_8. In addition to the previously studied octaazacubane structure (O_h symmetry), they investigated a D_{2d} strcture analogous to cyclooctatetraine, and a planar bicyclic form analogous to pentalene. Tian *et al* [17] investigated, in addition to O_h symmetry, two new structures of D_{2h} and C_{2v} symmetry, without N=N double bonds.

According to the above discussion, only the stability and structure of octaazacubane were searched from different theoretical point of view. But the electronic spectrum of octaazacubane is not found in the literature. This stimulated us to take into account of the electronic spectrum of octaazacubane. In this work, we have studied the spectrum of octaazacubane (O_h symmetry) at the SCF level of theory using STO basis set. The method employed in this work, can be found in Ref. [18].

The optimized geometry of N_8 (R = 1.525 A°) which was determined and characterized at the correlated level by Lauderdale *et al* [1], was used in this work.

Tables 1–3 contain the computed results of octaazacubane. Table 1 contains ionization potentials deduced from Koopmans theorem and the orbital symmetries. Table 2 contains singlet excitation energies, oscillator strengths and the symmetries of the excited states. The last column of Table 2 contains the percentage Rydberg character of the states. Table 3 gives transition energies, symmetries of the excited states and singlet-triplet splittings. The last column of Table 3 gives the percentage Rydberg character of the states.

Table 1. The lowest ionization potentials of octaazacubane (eV).

Molecule	MRINDO/S		
(Symmetry)	I.P.	Symmetry of orbital	Type
N_8	11.197	t_{1g}	π
(O_h)	11.199	a_{2g}	σ
	13.027	t_{1u}	π
	13.040	a_{2u}	σ
	14.385	t_{2g}	π
	14.404	t_{1u}	π
	15.811	a_{1g}	σ
	17.496	a_{1u}	σ
	18.425	a_{1g}	σ
	18.450	t_{2u}	π
	22.874	a_{2g}	σ
	22.878	a_{1g}	σ
	31.390	e_g	σ
	31.394	a_{2u}	σ

Table 2. Lowest singlet excitations in octaazacubane. All energies are in eV

Molecule	MRINDO/S				%Rydberg character
(Symmetry)	Transition energy	f	Sym. of excited state	Type	N
N_8	5.842	0.000	T_{2u}	$n \rightarrow \sigma^*$	0
(O_h)	5.847	0.000	A_{1g}	$n \rightarrow \sigma^*$	0
	5.850	0.000	A_{1g}	$n \rightarrow \pi^*$	0
	5.857	0.000	A_{2g}	$n \rightarrow \sigma^*$	0
	5.867	0.000	T_{2g}	$n \rightarrow \pi^*$	0
	5.984	0.037	T_{2g}	$n \rightarrow \pi^*$	0
	6.066	0.036	A_{1u}	$n \rightarrow \sigma^*$	0
	6.102	0.026	T_{1g}	$n \rightarrow \pi^*$	0
	6.113	0.076	A_{2u}	$n \rightarrow \sigma^*$	0
	6.166	0.001	T_{2g}	$n \rightarrow \pi^*$	0
	6.174	0.010	A_{2u}	$n \rightarrow \sigma^*$	0
	6.361	0.000	T_{1g}	$n \rightarrow \sigma^*$	1
	6.363	0.000	T_{2u}	$n \rightarrow \pi^*$	1
	6.407	0.000	T_{2g}	$n \rightarrow \pi^*$	1
	6.408	0.000	A_{1g}	$n \rightarrow \sigma^*$	1
	6.411	0.001	A_{1u}	$n \rightarrow \sigma^*$	1
	6.412	0.001	A_{2u}	$n \rightarrow \sigma^*$	1
	6.508	0.000	A_{1g}	$n \rightarrow \pi^*$	0
	6.584	0.004	A_{2g}	$n \rightarrow \sigma^*$	0
	6.600	0.000	T_{2g}	$n \rightarrow \pi^*$	0
	6.610	0.000	A_{1g}	$n \rightarrow \pi^*$	0
	6.621	0.002	A_{2g}	$n \rightarrow \sigma^*$	0
	6.896	0.069	T_{2g}	$n \rightarrow \pi^*$	0
	7.087	0.002	A_{2g}	$n \rightarrow \sigma^*$	0
	7.101	0.011	T_{2g}	$n \rightarrow \pi^*$	0
	7.393	0.000	A_{1g}	$n \rightarrow \sigma^*$	1
	7.436	0.001	T_{1g}	$n \rightarrow \pi^*$	0

Ionization potentials :

The first ionization potential of octaazacubane is interpreted as the removal of an electron from a π orbital while the second one as the removal of an electron from a σ orbital. A comparison of these two ionization potentials reveals that both π and σ electrons have approximately the same tendency to leave the molecule. Again, comparing the third and the fourth ionization potentials, a similar tendency is found for both π and σ electrons to leave the

Table 3. Triplet excitations in octaazacubane. All energies are in eV.

Molecule	MRINDO/S				%Rydberg character
(Symmetry)	Transition energy	S-T split	Sym. of excited state	Type	*N*
N_8	5.375	0.609	T_{2g}	$n \rightarrow \pi^*$	0
(O_h)	5.377	0.736	T_{1g}	$n \rightarrow \pi^*$	0
	5.510	0.332	T_{2u}	$n \rightarrow \sigma^*$	0
	5.546	0.556	T_{1g}	$n \rightarrow \pi^*$	0
	5.555	0.302	A_{2g}	$n \rightarrow \sigma^*$	0
	5.613	0.237	A_{1g}	$n \rightarrow \pi^*$	0
	5.617	0.230	A_{1g}	$n \rightarrow \sigma^*$	0
	5.628	0.239	T_{1g}	$n \rightarrow \sigma^*$	0

molecule. This in turn, implies that the $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions would be of comparable intensity in octaazacubane. This aspect of the octaazacubane spectrum is discussed in the succeeding section.

Singlet excitations :

The lowest singlet excitation in octaazacubane is predicted at 5.842 eV. Thus, the octaazacubane spectrum cannot be expected in the visible or in the near-ultraviolet, for it appears in the medium ultraviolet under the approximation used in this work. The first absorption in octaazacubane takes place at 5.984 eV. The transition corresponding to this absorption is assigned as $n \rightarrow \pi^*$ which has an oscillator strength of 0.037. Several allowed transitions are reported between 5.984 and 6.174 eV, the one at 6.133 eV is the most intense (f = 0.076) transition throughout the spectrum of octaazacubane. Thus, this energy corresponds to the maximum absorption in octaazacubane. The transition corresponding to the maximum absorption is assigned as $n \rightarrow \sigma^*$. Allowed transitions are also found in the shorter wavelength side of the spectrum. $n \rightarrow \pi^*$ transition at 6.986 eV has an oscillator strength of 0.069. A comparison of oscillator strength of this $n \rightarrow \pi^*$ transition with that of the maximum absorbing $n \rightarrow \sigma^*$ transition (f = 0.076) reveals that these transitions are of comparable intensity and can be observed experimentally because they are adequately spaced and in addition, the former is x-polarized while the latter is y-polarized.

In the present calculation, we used an extended basis set (which includes Rydberg atomic orbitals into the valence basis set), but we notice that the spectrum of octaazacubane is devoid of Rydberg excitations.

Triplet excitations :

The lowest triplet transition in octaazacubane is assigned as $n \rightarrow \pi^*$ at 5.375 eV. This triplet is separated from its corresponding singlet by an energy of 0.609 eV. As to the singlet-triplet splittings, the splittings for $n \rightarrow \pi^*$ transitions are higher by about twice the splittings for $n \rightarrow \sigma^*$ ones. The $n \rightarrow \pi^*$ transitions in octaazacubane exhibit intensity. All the triplet excitations are entirely valence shell type because they have zero percent Rydberg character. We are unable to compare our results due to the lack of any other relevant theoretical or experimental data in the literature.

The electronic spectrum of octaazacubane has not yet been observed or theoretically calculated in the literature. Our calculation reveals that the spectrum of octaazacubane is compact. Nevertheless, the structural features of the spectrum of octaazacubane are well pronounced. We hope that the present results would be helpful in futher studies.

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